High Energy Density Lithium/Sulfur Batteries for NASA and DoD Applications

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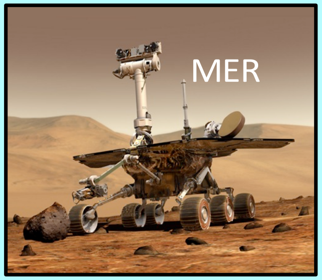
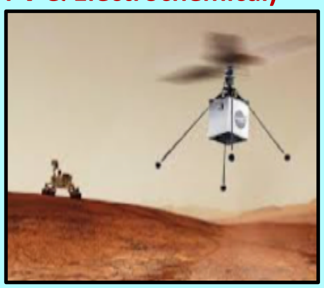
Types of Planetary Missions

Planetary Missions

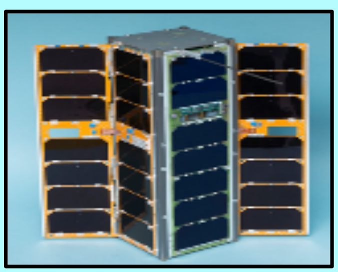
Flyby or Orbiter (RPS/PV & Electrochemical



Lander or Rover (RPS/PV & Electrochemical)



Probes (Electrochemical) Aerial (PV & Chemical)



Cubesat (PV & Chemical)

Extra Vehicular Activities

Need for Wh/kg & Wh/l Increase

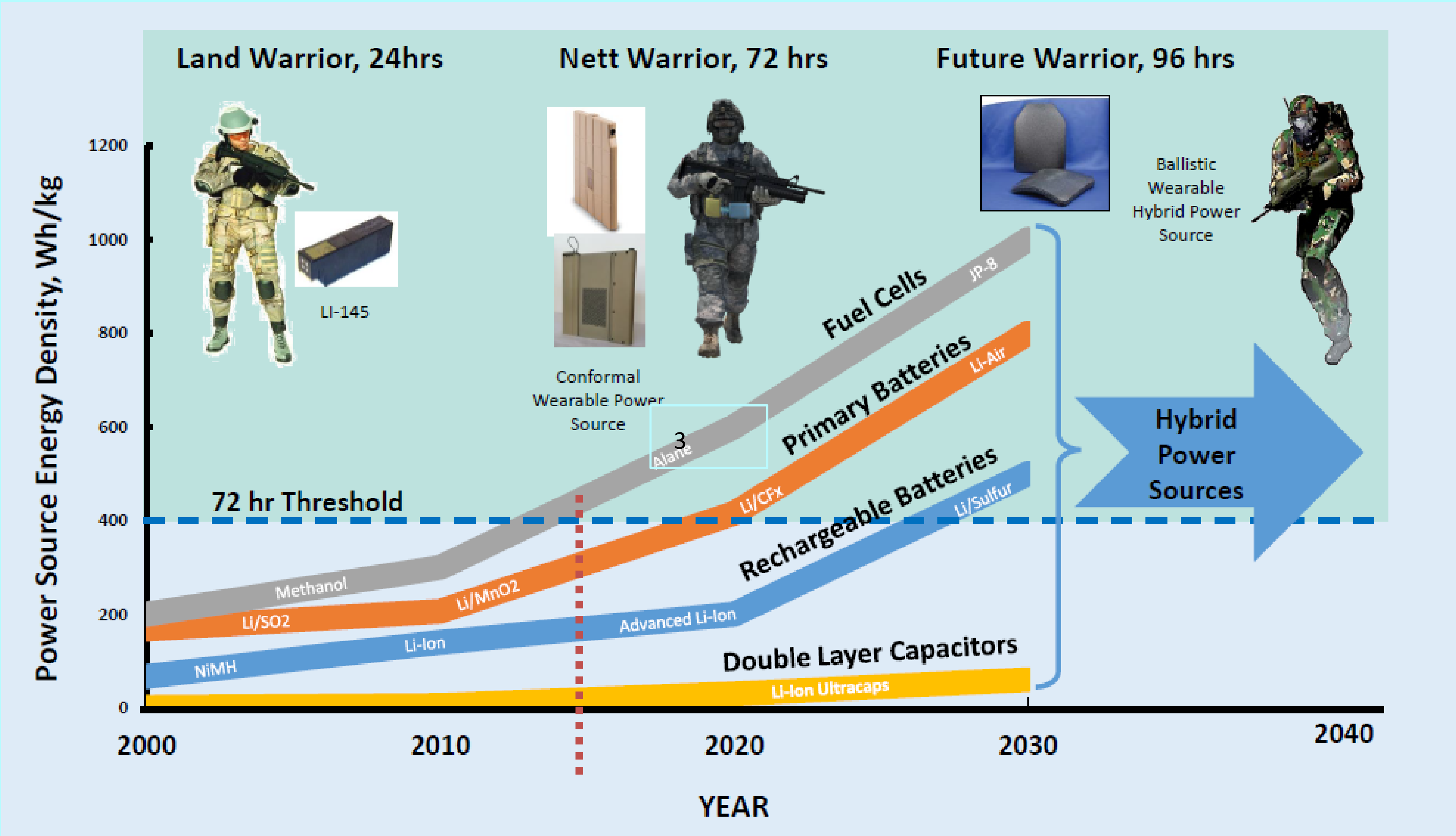
Technology Drivers

- High Specific energy
- High Energy Density
- Good Low temperature Performance
- Long Calendar Life
- Low Self Discharge
- Safety and
- High reliability

Need for Cycle life Increases

Pre-decisional: for information and discussion purposes only

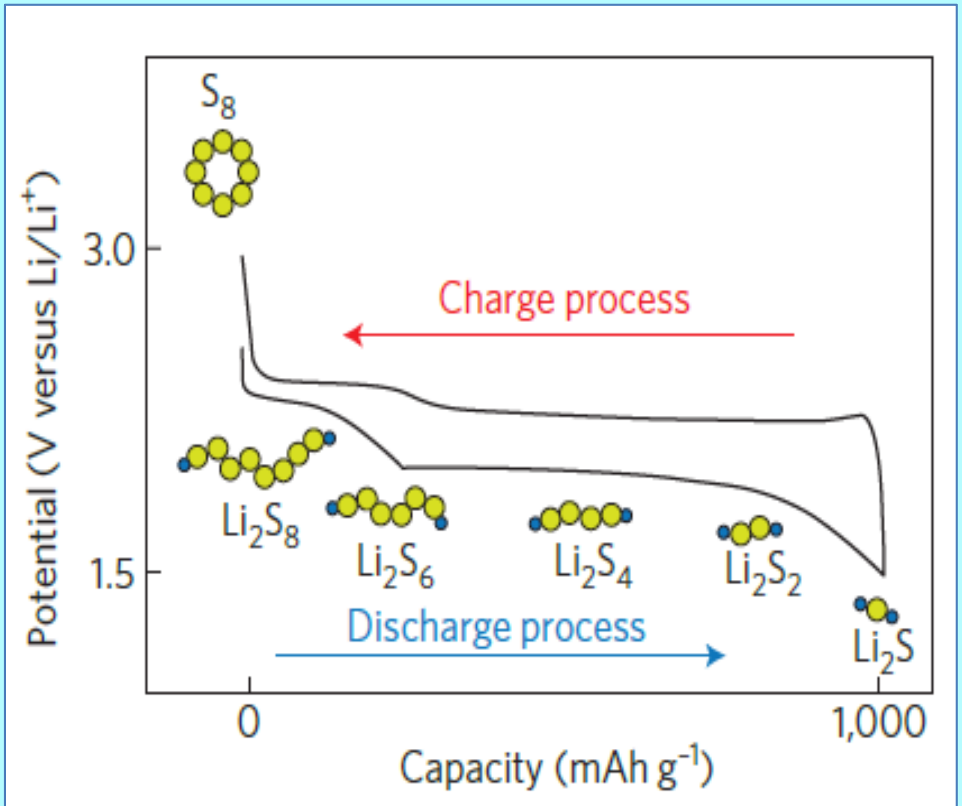
DoD Applications- Soldier Power Trends



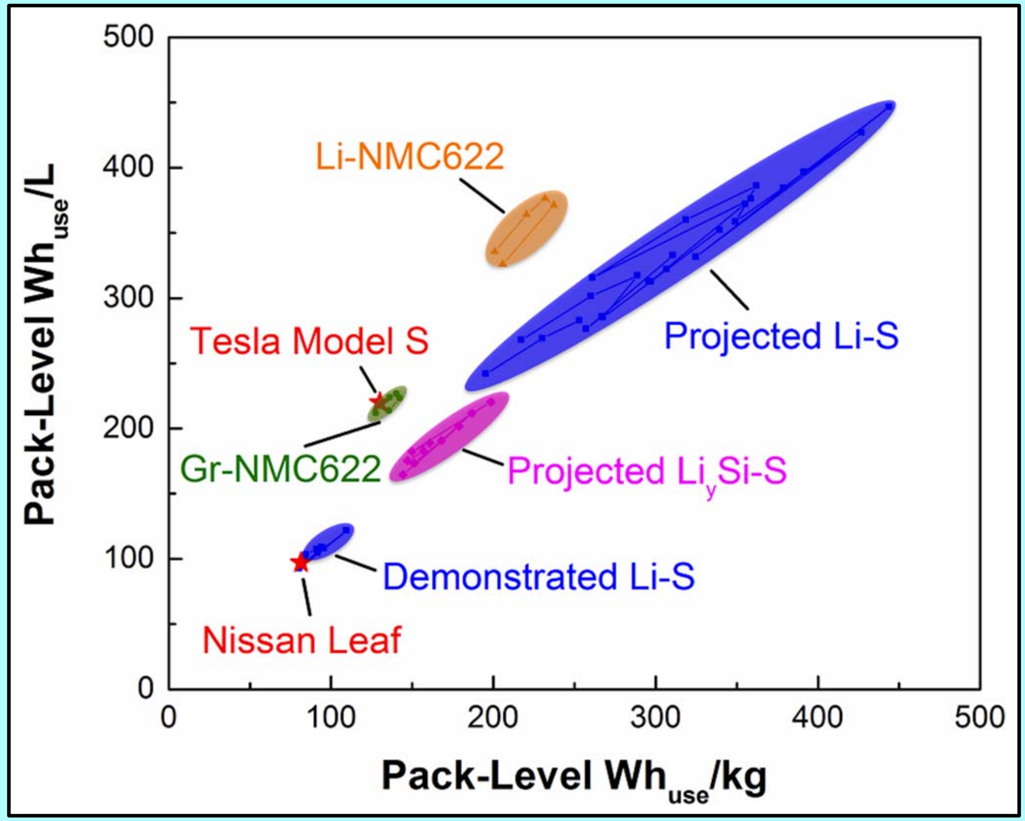
- Lithium-sulfur chemistry is expectedly the next-generation rechargeable battery technology for soldier power needs

Why Lithium-Sulfur Batteries?

Sulfur Cathode



Energy Projections

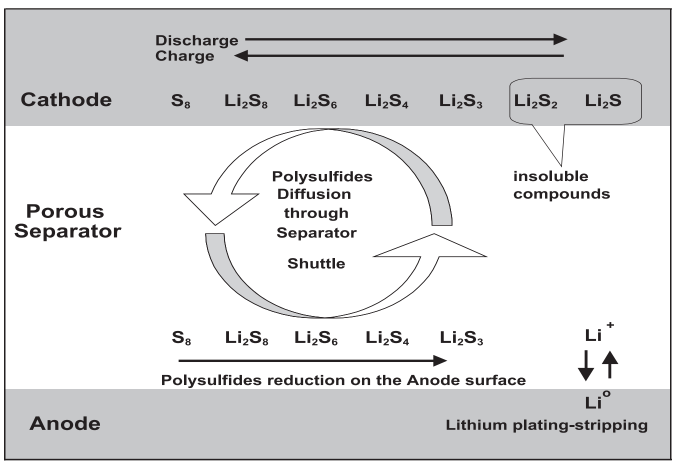


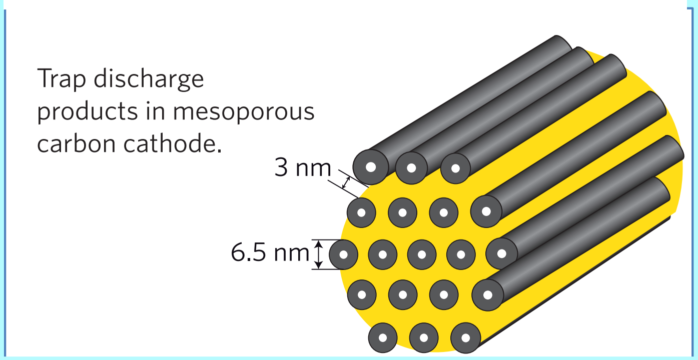
- High specific capacity of 1670 mAh/g; High theoretical specific energy of 2567 Wh/kg
- 250-400 Wh/kg realized in practical cells.
  - Higher specific energy cells have generally shorter cycle life

Projected pack-level Wh/kg and Wh/l for a 100 kWh, 80 kW and 360 V Li-S battery with higher loadings (>8 mAh/cm^2 and 7 mg S/cm^2) vs. estimated from demonstrated cell performance (~2.5 mAh/cm^2 and 2 mg S/cm^2)

Gallagher et al JECS, **162** (6) A982-A990 (2015)

Life-limiting Processes in a Li-S cell and the Mitigation Strategies





- Anode passivation and dendrite formation.
- Sulfur expands by 79%
- Poor conductivity of S and its discharge products.
- Polysulfides are soluble in many solvents : Form Redox shuttle and insulating layer (Li_2S) on the anode

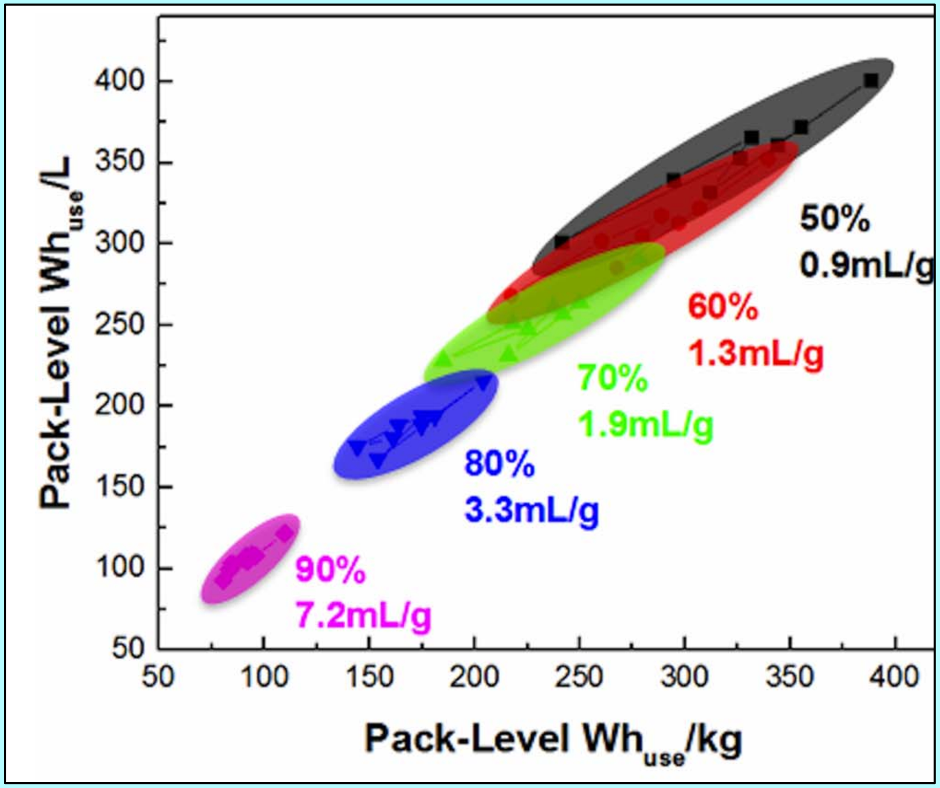
Problems	Strategies Adopted	Rationale
Poor cyclabaility and dendrites	Coat with protecting layer (solid electrolyte)	Blocks contact between Li and soluble sulfide species and/or mechanically inhibit Li dendrites
	Coat with protecting layer (gel polymer)	
Polysulfide dissolution, redox shuttle behavior	Immobilize in carbon host matrix	Strong S-C interactions trap sulfides (e.g. as S_n^{x-} chain-like species, as cyclo-S_8 allotrope does not fit inside pores)
	Use sulfide (discharge product) as cathode	Allows use of non-Li anodes
Poor Conductvity and expansion	Meso/microporous carbon support for S	High electronic conductivity of C mitigates poor S conductivity
Passivation	Use sulfide (discharge product) as cathode	Allows use of non-Li anodes
Soluble sulfides affecting anode stability and performance	Organic electrolyte with additives (e.g. $LiNO_3$, P_2S_5)	Good conductivity, additives react preferentially with sulfide species and passivate Li surface, depassivate cathode
	Ionic liquid electrolyte	Sulfides are insoluble in certain ionic liquids
	Solid-state electrolyte	Blocks contact between Li and soluble sulfide species and/or mechanically inhibit Li dendrites

- **Some of these approaches have shown improved cycle life, but only with low sulfur loadings (2-3 mg/cm²)**

Design Considerations for a 400 Wh/kg Li-S cell

Cathode Loading

- Cathode loading in a Li-ion cell (nickel cobalt aluminum oxide, NCA): ~15 mg/cm^2, i.e., ~2.23 mAh/cm^2 or 8.9 mWh/cm^2 per side
- For 400 Wh/kg, i.e.,1.5 times the specific energy vs. Li-ion cells, i.e., 13 mWh/cm^2 per side.
- With a voltage of 2.1 V for Li-S cell, this implies an areal capacity of ~6.2 mAh/cm^2 for the sulfur cathode.
- With 800 mAh/g from sulfur (and with a composition of 65% sulfur), the required loading is 12 mg/cm^2.
- Almost all reports of Li-S cells in the literature describe performance of sulfur cathodes with a low loading of < 5mg/cm^2 (mostly 2-3 $mg.cm^{-2}$) and/or with low proportion of sulfur in the cathode.



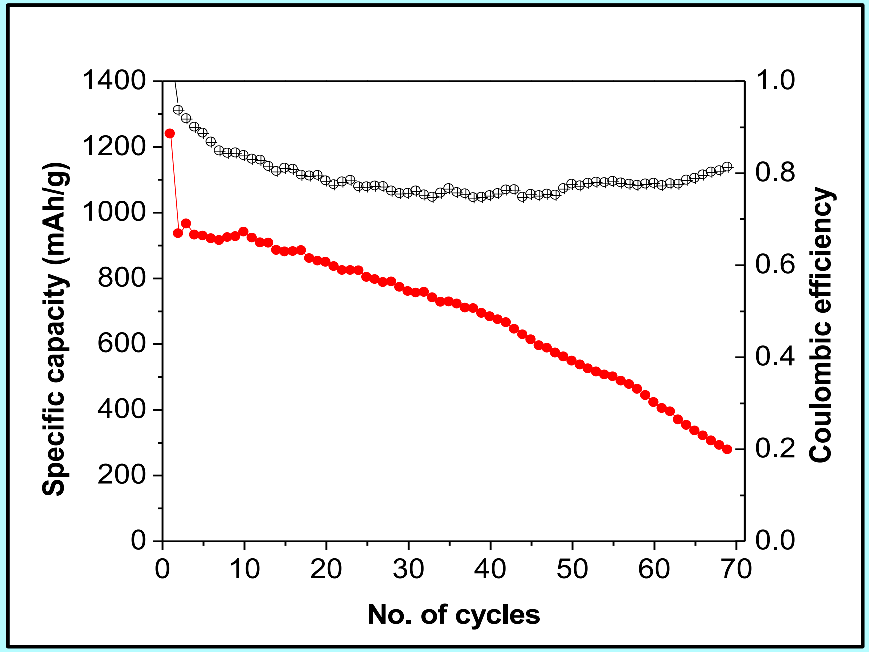
- Electrolyte content needs to be reduced to 4-5 ml/g (currently 9-13 ml/g of S)

Our Approach to High Capacity and Long-life Li-S cells

- Baseline Li-S cells have poor cycle life (capacity fade and low efficiency)
- Our strategies to improve the cycle life sulfur cathodes with high loadings:
  - Modification of sulfur cathode with metal sulfide blends
  - Coating of separator with ceramic compounds (Al_2O3 and AlF_3) and polymeric materials.
  - Protection of Li anode with ALD-deposited AlF_3
  - Assessment of high concentration electrolytes
  - Corroboration with in-situ polysulfide determination

S: C: PVDF (55: 40:5) 6 mg/cm²

1.0MLiTFSI+ DME (Dimethoxy Ethane) +DOL (Dioxolane) (95:5) with a Carbon Cloth



- Lower capacity and utilization of sulfur in thicker cathode even with carbon cloth interlayer and $LiNO_3$.
- With denser sulfur cathodes, more polysulfides are expected to dissolve in the electrolyte.

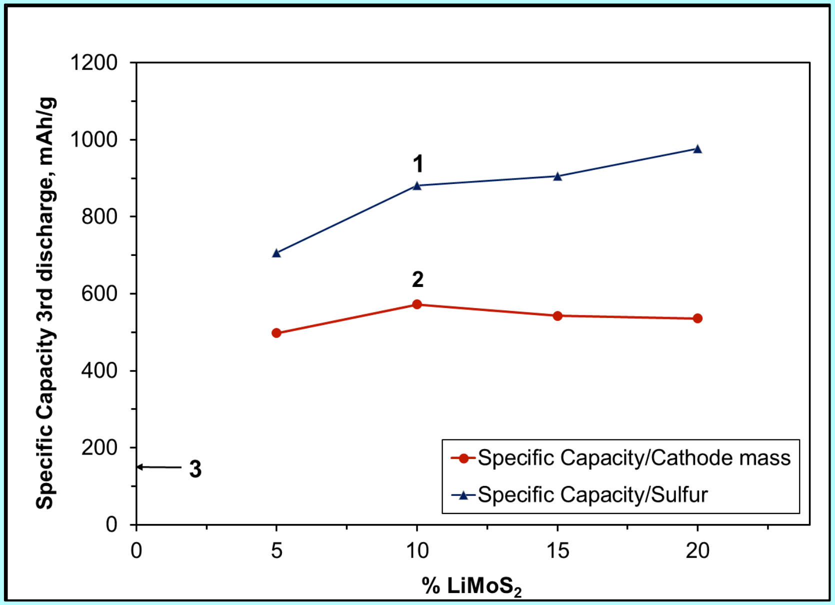
Metal Sulfide Blended S Cathodes

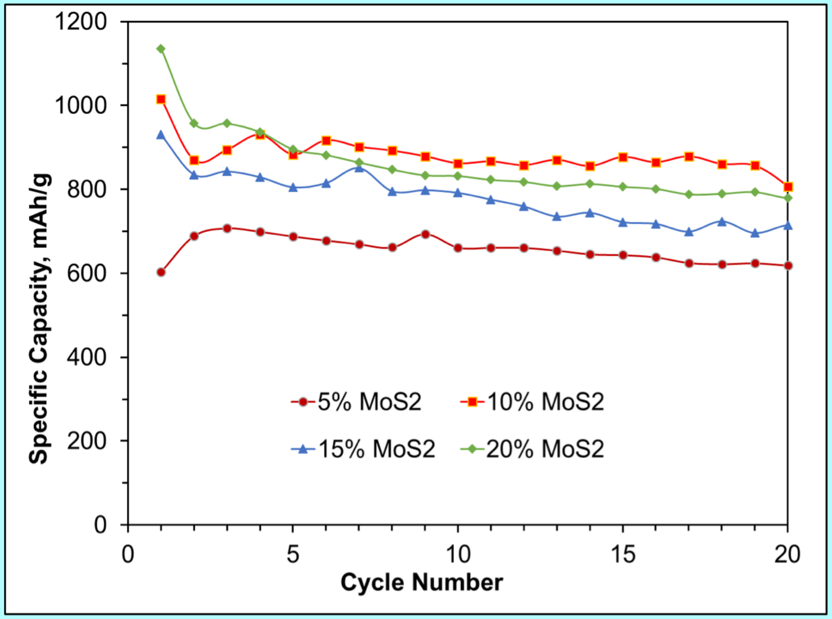
- Transition metal sulfide undergoes reversible reactions around the same voltage range and can add to the cathode capacity and also mediate the sulfur redox reaction.
  - TiS_2 (Manthiram et al), VS_2, ZrS_2 (Cui et al) with low loadings (<5mg/cm^2), CuS_2 (Takeuchi et al)
- Metal sulfide provides some electronic/ionic conductivity
- Easier to make dense electrodes
- Physical/Chemical Entrapment of S (Cui et al: Nature material Nature Communications 2014 | 5:5017 | DOI: 10.1038)
  - Strong Li–S interaction (between the Li atoms in Li_2S and S atoms in TiS_2), as well as strong S–S interaction between the S atoms in Li_2S and S atoms in TiS_2).
    - The binding energy between Li_2S and a single layer of TiS_2 was calculated to be 2.99 eV (10x vs Li_2S and a single layer of carbon-based graphene, a common encapsulation material).
    - Stronger interaction between Li_2S and TiS_2 can be explained by their similar ionic bonding and polar nature, unlike graphene which is covalently bonded and nonpolar in nature.
    - Entities that bind strongly to Li_2S exhibit strong binding with Li_2S_n species as well owing to their similar chemical bonding nature.

Screened several sulfides : TiS_2, MoS_2 have shown to to improve sulfur utilization and cycle life

Sulfur Cathode With Different amounts of MoS_2

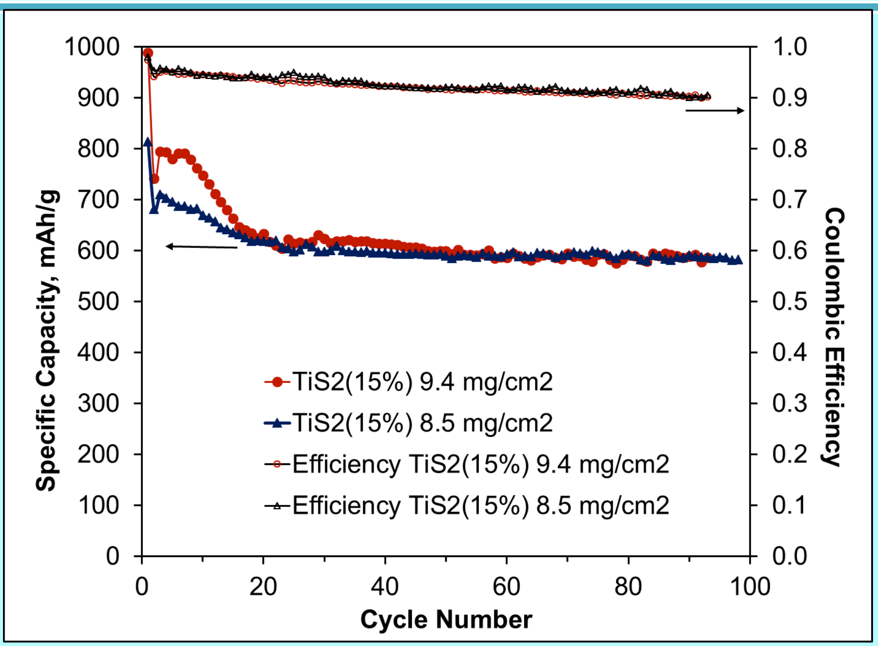
- The ratios of S and MoS_2 were varied from 55:20, 60:15, 65:10 and 70:5, while keeping the carbon and PVDF binder the same at 20% ad 5%, respectively (55:20:20:5, 60:15:20;5, 65:10:20:5 and 70:5:20:5 for S:MoS2:C:PVDF at ~9 mg/cm^2 (compared to Li-ion cathode powder, NCA)
- Specific capacity of sulfur increases with MoS_2 loading, but specific capacity of total cathode decreases at high loadings.
- High sulfur utilization and capacity retention during cycling with 10-15% of MoS_2 in the cathode (65% sulfur)

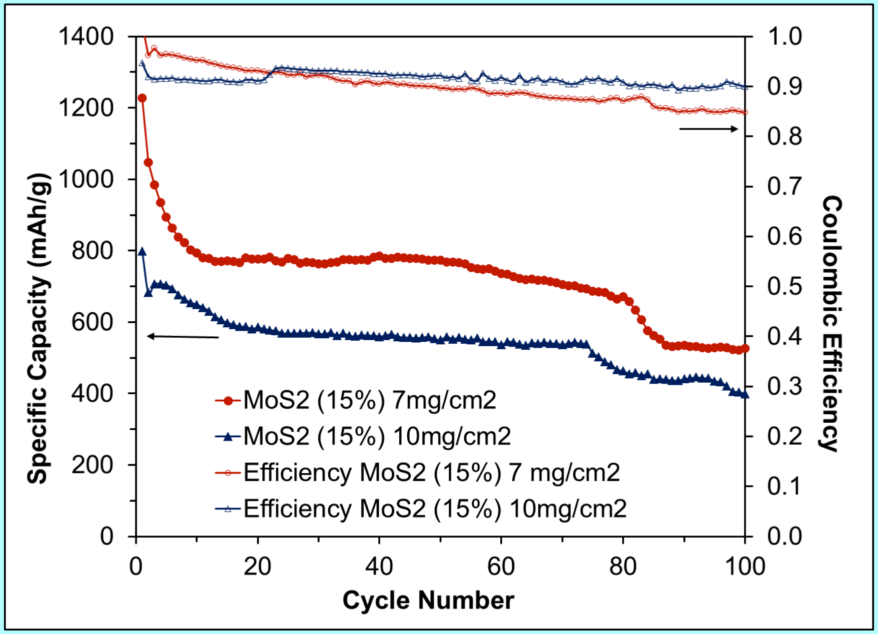




TiS_2- MoS_2 Blended Sulfur Cathode

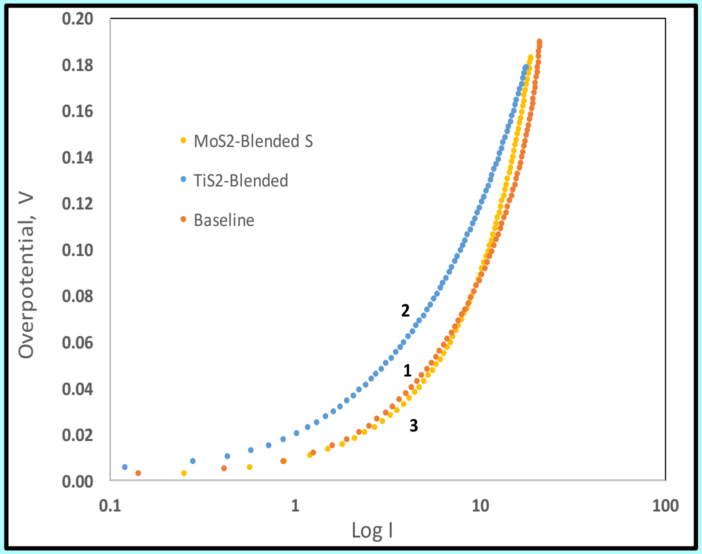
- Good performance considering the high cathode loading and high proportion of sulfur (4.6 mAh/cm^2 per side)
- High coulombic efficiency suggests polysulfide trapping.
- The XRD spectra for TiS_2 electrodes showed a transition from TiS_2 to $LiTiS_2$ after discharge and transition from $LiTiS_2$ to TiS_2 after charge.
- Similar to the baseline and MoS_2 electrodes the S-MoS_2 cathode showed the presence of sulfur peaks after charging and disappearance of the same peaks after discharging.
- No change in the MoS_2 peaks





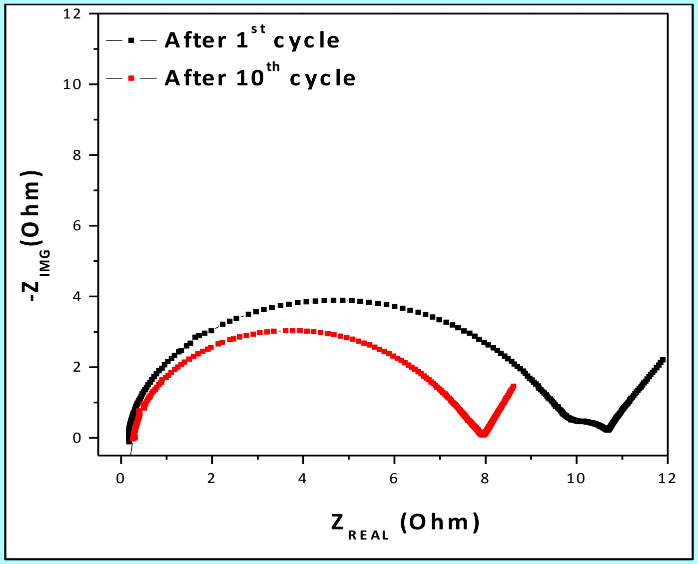
Kinetics of Sulfur Cathode

Kinetics Tafel Polarization

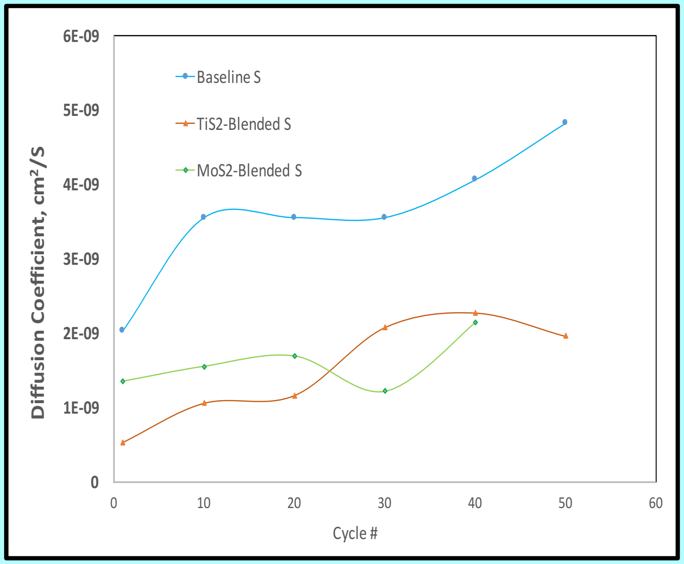


- Identical kinetics for sulfur reduction
- The exchange current density of pristine sulfur cathode is 0.19 mA/cm^2. In contrast, the exchange current densities of the composite cathodes with TiS_2 and MoS_2 blends are 0.21 mA/cm^2 and 0.23 mA/cm^2, respectively

EIS of MoS_2-Blended S Cathode



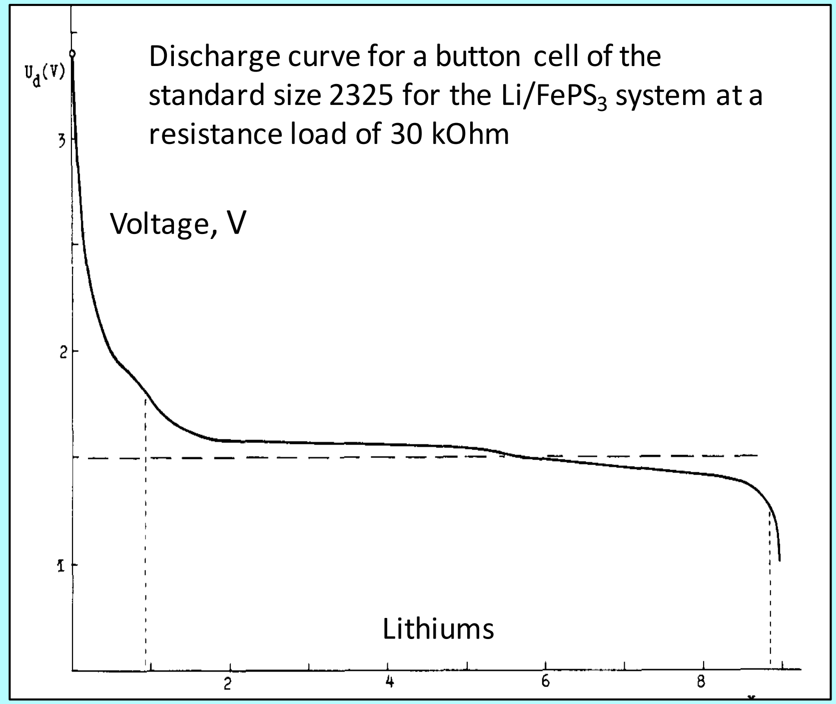
- Stable interface and lower impedance upon cycling



- Similar kinetics for Li diffusion in the cathodes.

Metal Phosphorus Trisulfides for Composite Sulfur Cathodes

- Rationale: Involve reactions with multiple lithiums in the same voltage range as the sulfur cathode
- Synthesis: 'one-zone' heating at 973-1023 K of a stoichiometric mixture of suitable components in evacuated ampoules for five and more days followed by a very slow cooling
- Synthesized several metal trisulfides: $FePS_3$, $NiPS_3$, $CoPS_3$ and $MnPS_3$. Composition confirmed from XRD

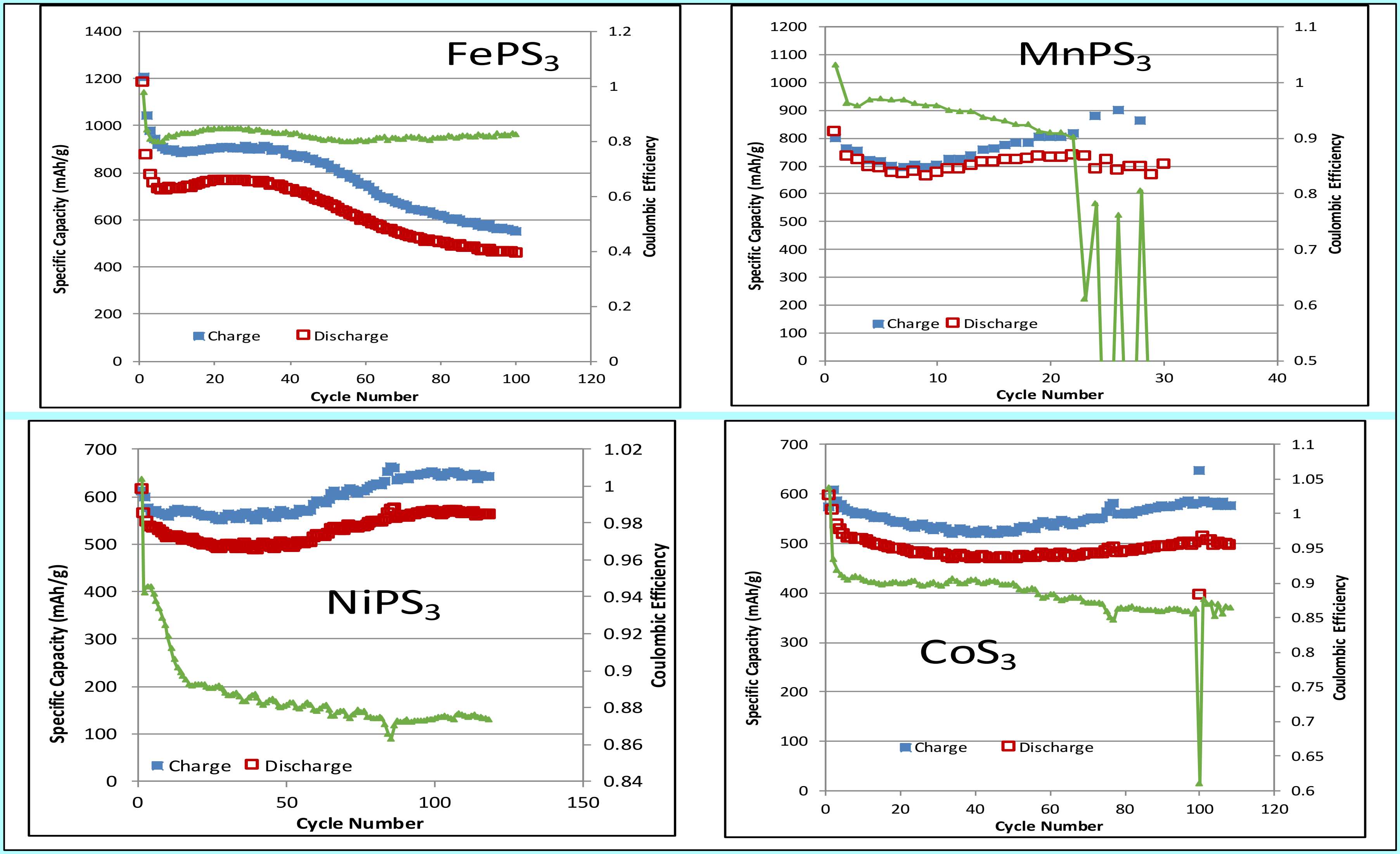


$$2\mathrm{Li} + \mathrm{MPX}_3 \rightleftarrows \mathrm{Li}_2\mathrm{MPX}_3$$

Two lithiums (reversible) and nine lithiums (irreversible)

Kuzminskii et al, J. Power Sources, 55, 133 (1995)

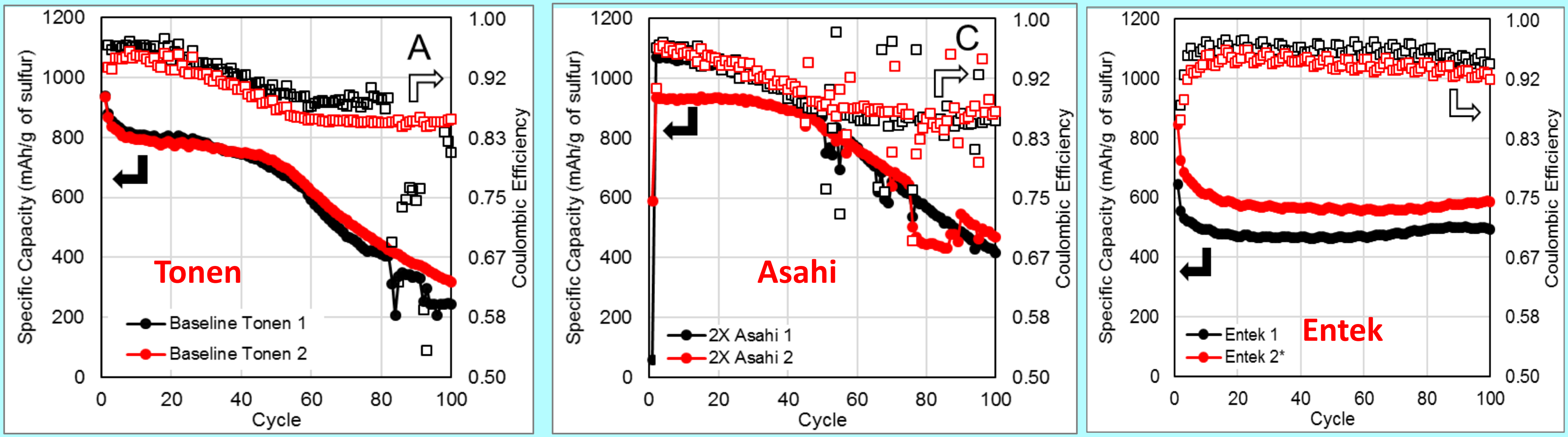
Metal Phosphorus Trisulfides for Composite Sulfur Cathodes



Composition:(S:MPS_3:C:PVDF=65:15:15:5); loading 5 mg/cm^2

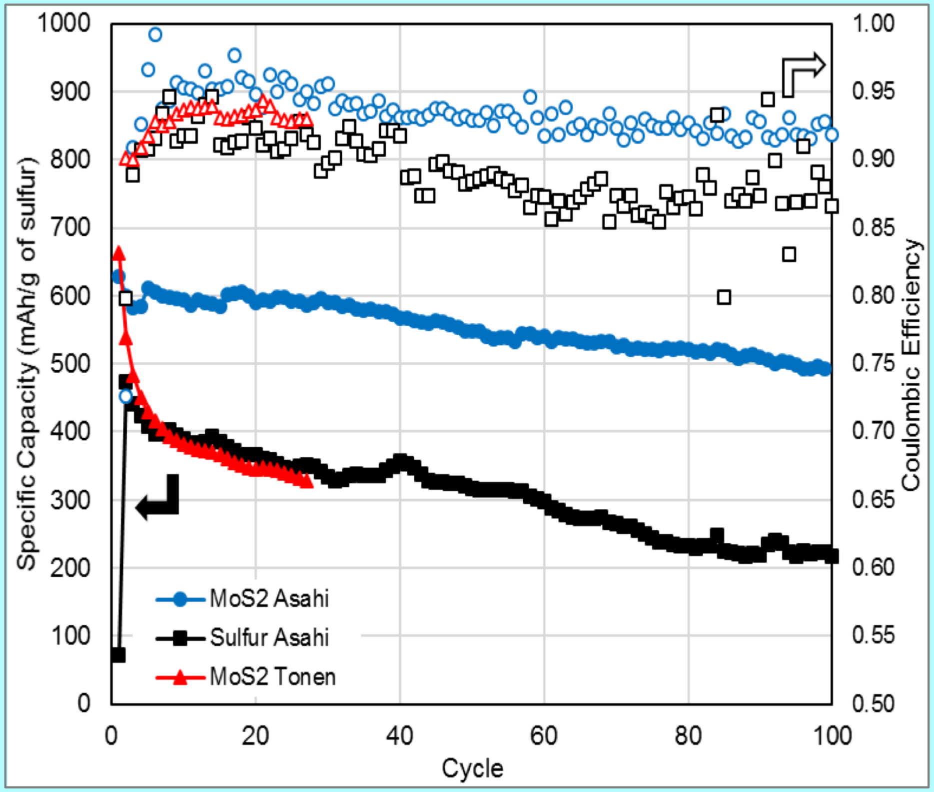
Li-S cells with Al_2O_3-coated separator (Asahi and Entek)

Tonen Separator **Al_2O_3 Coated –Two layers**



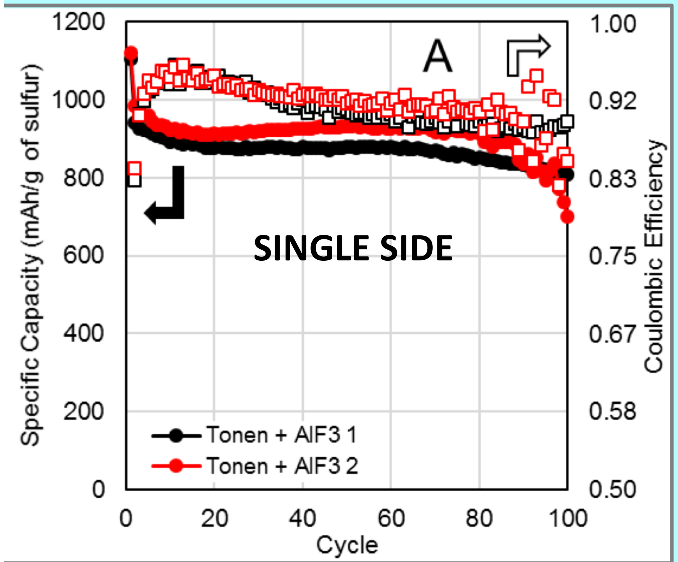
- Motivation:
  - Al_2O_3-coated Celgard separator blocks the diffusion of the polysulfide anions by physical adsorption and electrochemical deposition (Zhang et al., Electrochim. Acta 129, 55 2014)
  - Wixom et al (Navitas): Coating with Titanium nitride for aiding in the electrochemical reduction of polysulfides.
- Separator coated with Al_2O_3 on one side (typically used on the cathode side)
- Improved performance with two layers of Asahi separator
- Entek separator gives lower but stable capacity

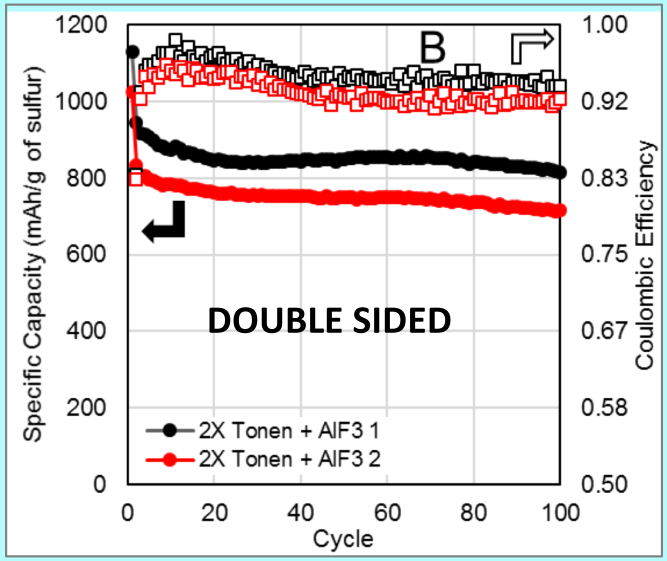
Li- S Pouch Cells

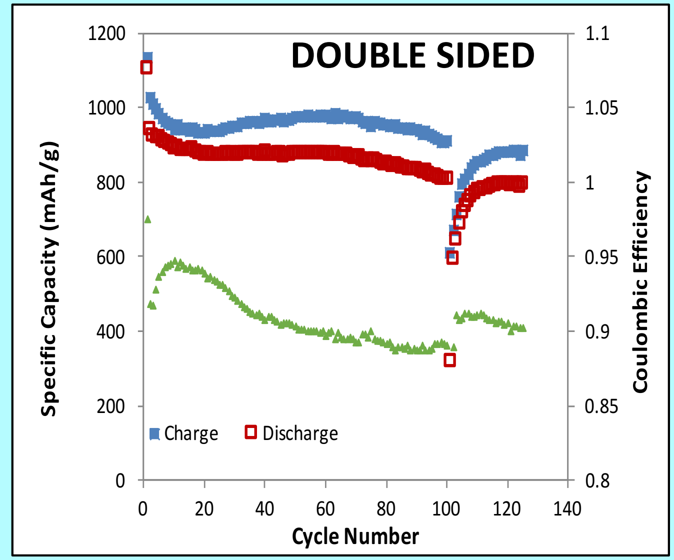


- Cell with S-MoS_2 cathode (10 mg/cm^2 loading) and Asahi separator outperforms Cell with baseline sulfur cathode (10 mg/cm^2 loading) and Tonen separator.
- Excellent performance with high sulfur content (65%) and loading (10 mg/cm^2) with MoS_2 blending (15%) and new separator
- 4mAh/cm^2 per side (8 mAh/cm^2 both sides) based on the realized capacity
- Electrolyte content is ~9 ml/g of S.

AlF_3-coated Tonen separator (spray coated)

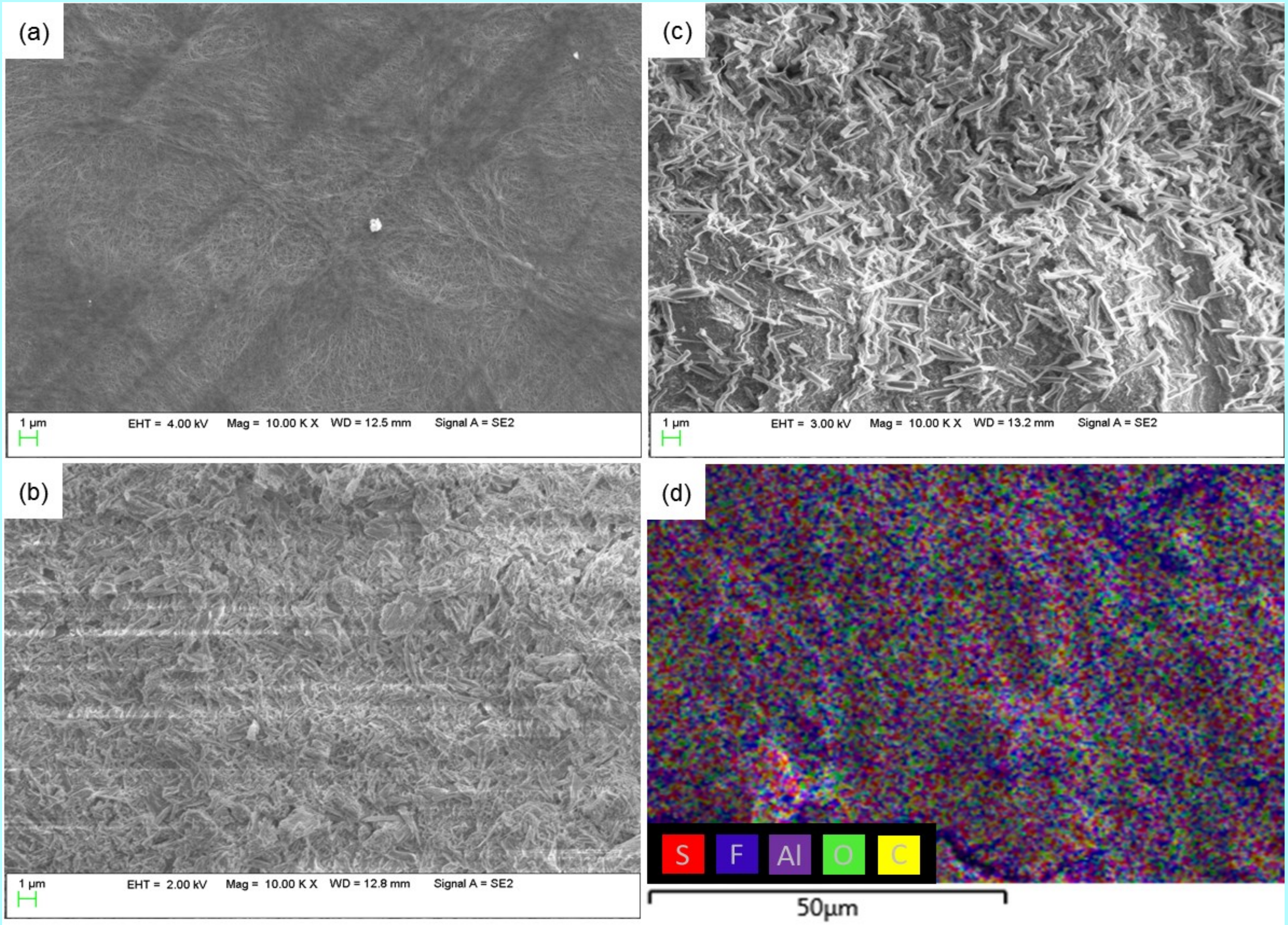






- AlF_3 is used as coating for high voltage cathodes in Li-ion cells.
- Li-S coin cells containing sulfur cathode of composition S:CB:PVDF(55:40:5), 6.45mg/cm^2 and AlF_{3}-coated Tonen separator (spray coated)
- Good cycle life with high coulombic efficiency
- Also, good capacity recovery after test interruption for 3 weeks

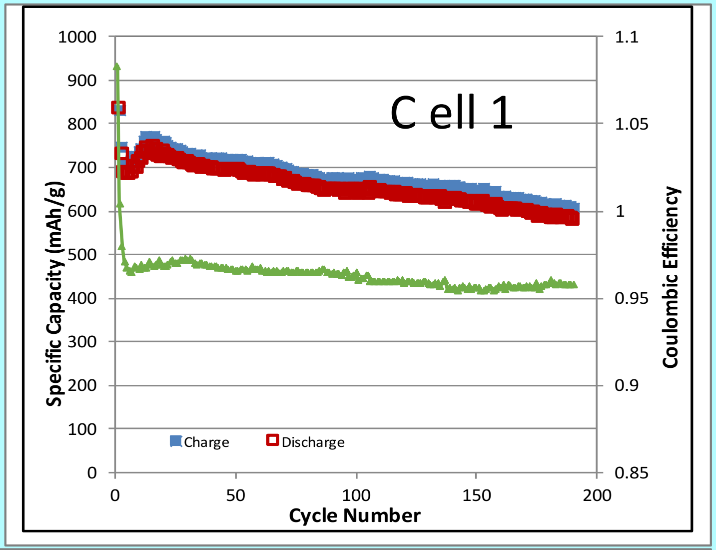
AlF_3-coated Separators from Cycled Cells

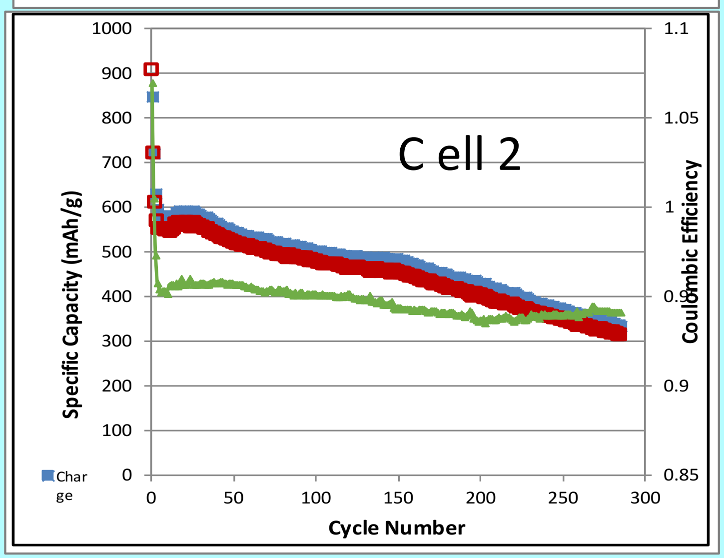


SEM images of (**a**) fresh Tonen separator, (**b**) Tonen separator coated with AlF_3 and (**c**) AlF_3-coated Tonen separator after 100 cycles showing AlF_3 material present on the surface after coating, and deposition of sulfur-containing species on the surface of these particles after cycling. EDS in (**d**) indicates approximately uniform distribution of sulfur-containing species across the surface of the coated separator.

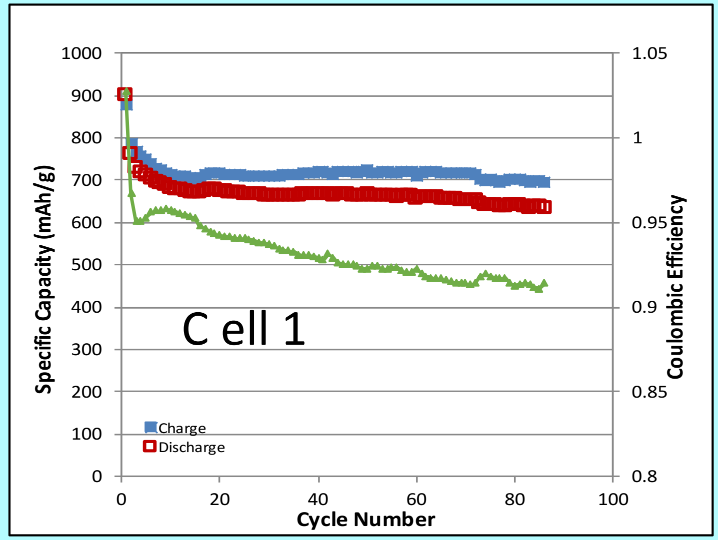
Li-S Coin cells with AlF_3-coated separator (doctor blade)

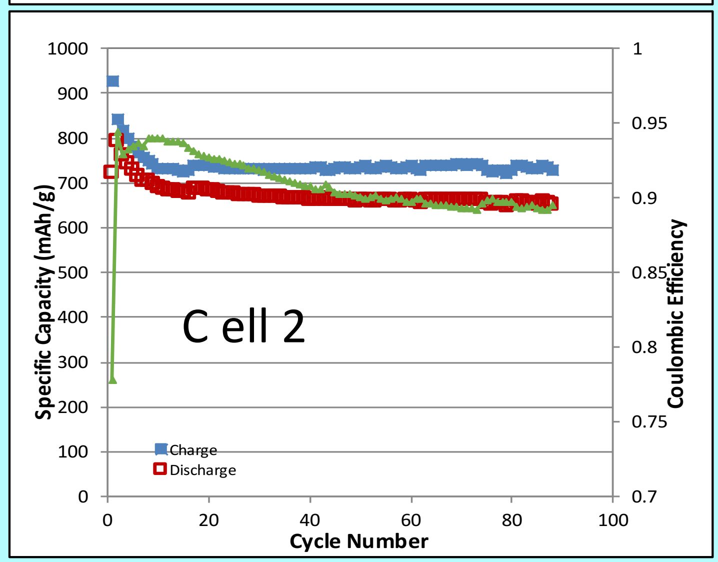
With 5% PVDF





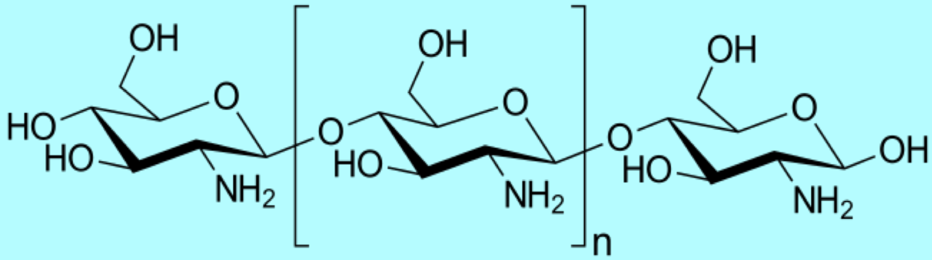
With 2% PVDF





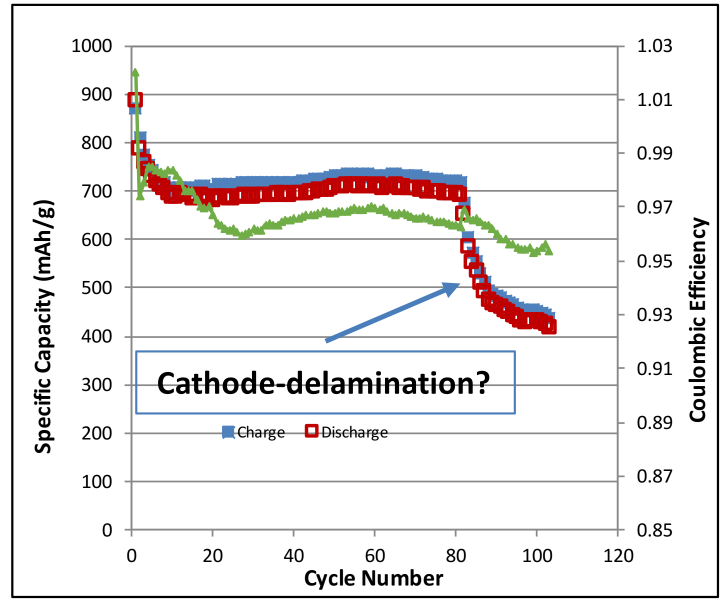
- Good cyclic stability and high coulombic efficiency
- The coating needs to be optimized to improve the initial capacity, may be with reduced binder content.
- Capacity has improved with 2% binder, binder the efficiency is lowered slightly (till over 90 %)

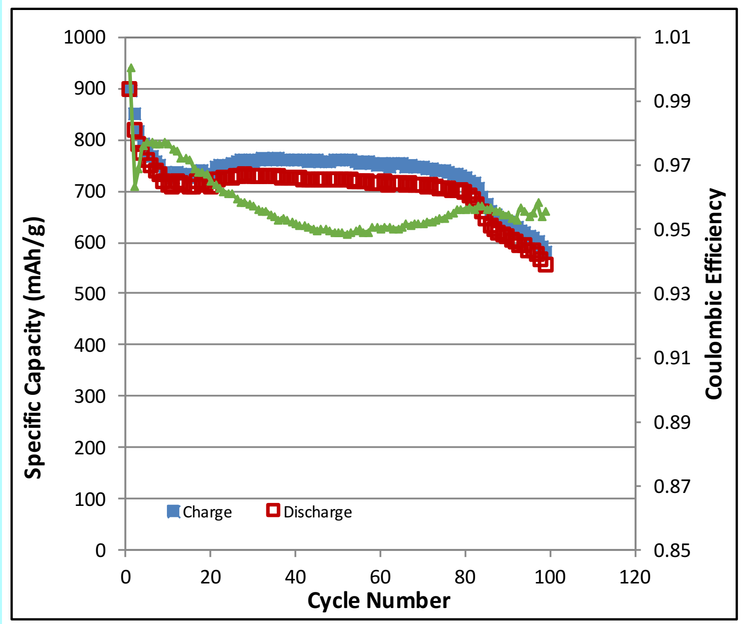
Li-S cells with Chitosan coated separator (Asahi)



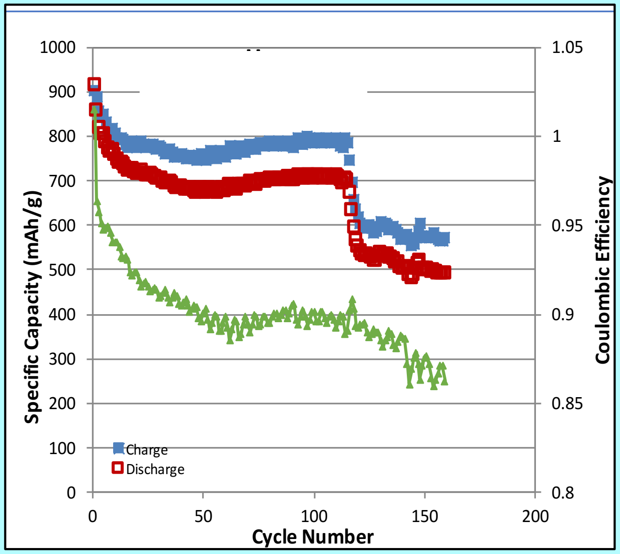
Commercially available polymer, used in agriculture and medicine,

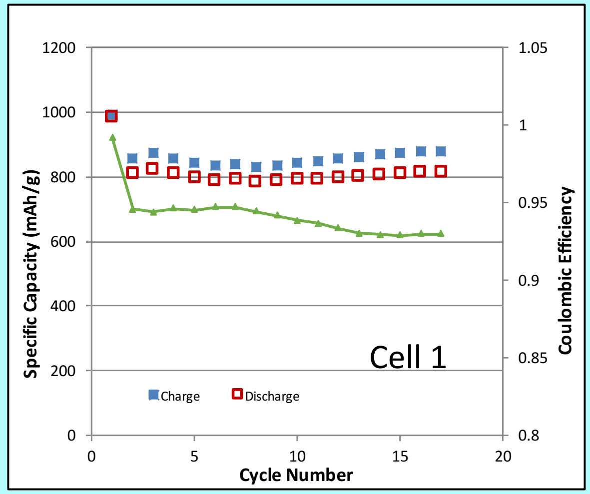
- Separator coated with Chitosan on one side (typically used on the cathode side) – Spin coated
- Stable cycle life with high coulombic efficiency
- Capacity drop observed after 80 cycles

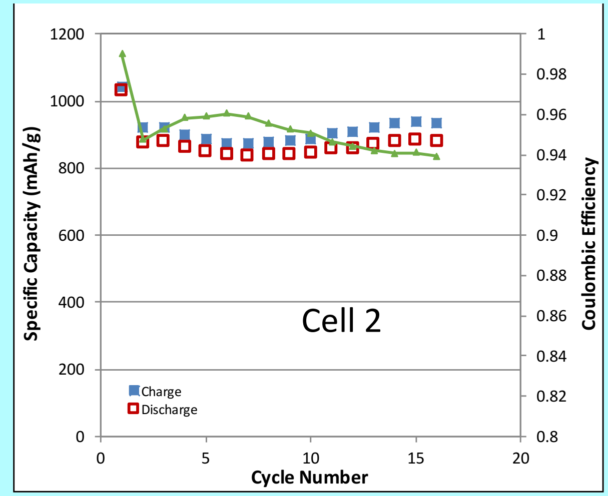




AlF_3-coated (ALD) Li Anode



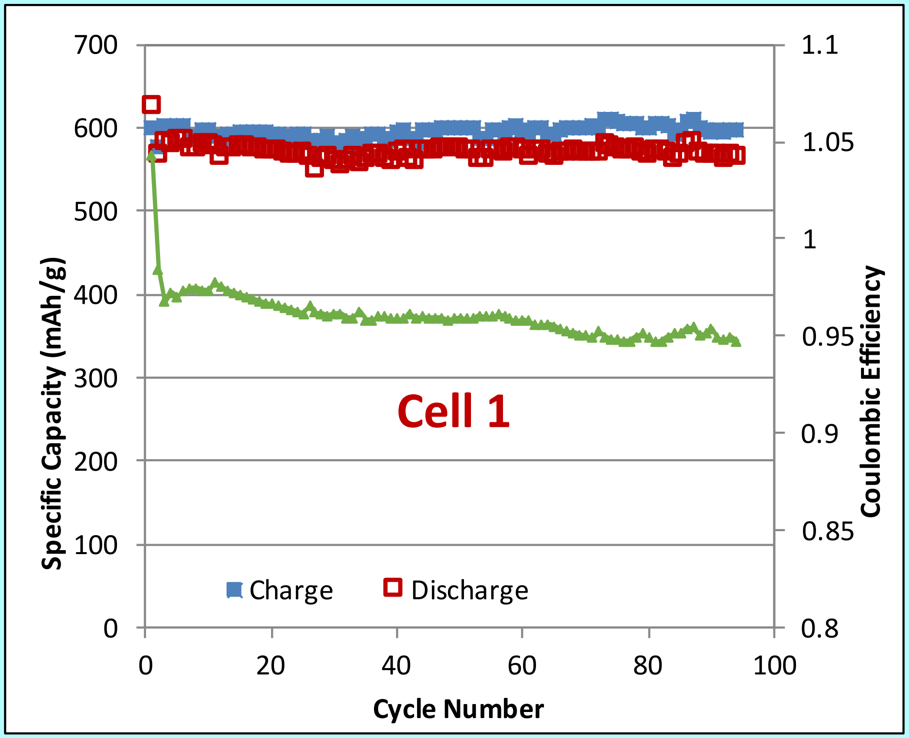


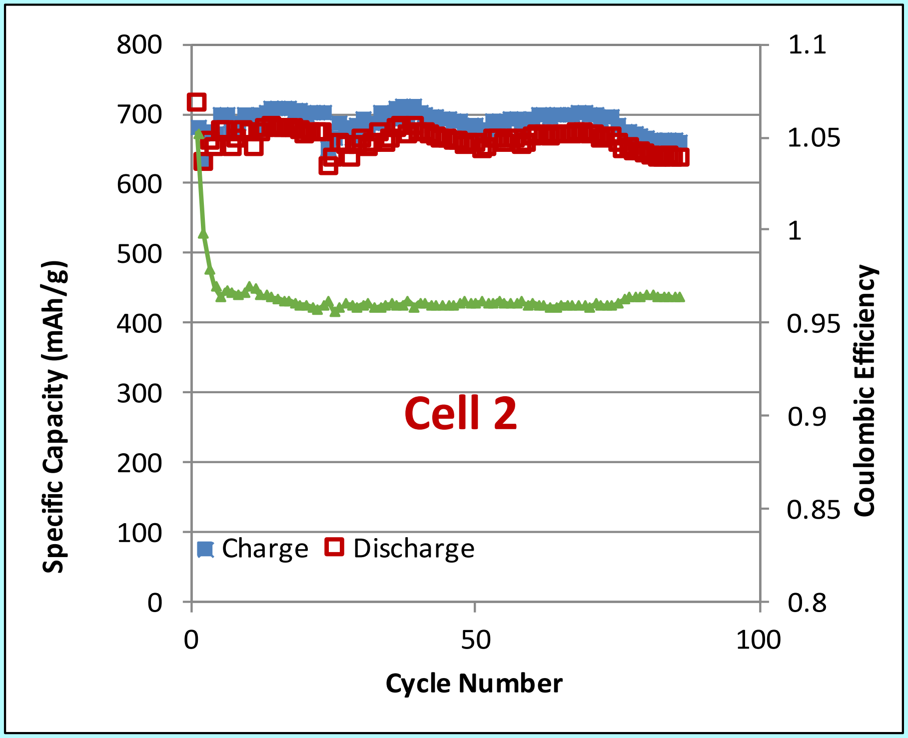


- Procedure: Pulse trimethyl aluminum $Al(CH_3)_3$ followed by HF in 40 times, which should have formed a 4.8 nm thick AlF_3 coating on Li based on calibration runs using on silicon wafers.

- Good performance with MoS_2-blended sulfur (65% with 15% MoS_2) at 11.2 mg/cm^2. High Sp. Capacity of 6 mAh/g per side.

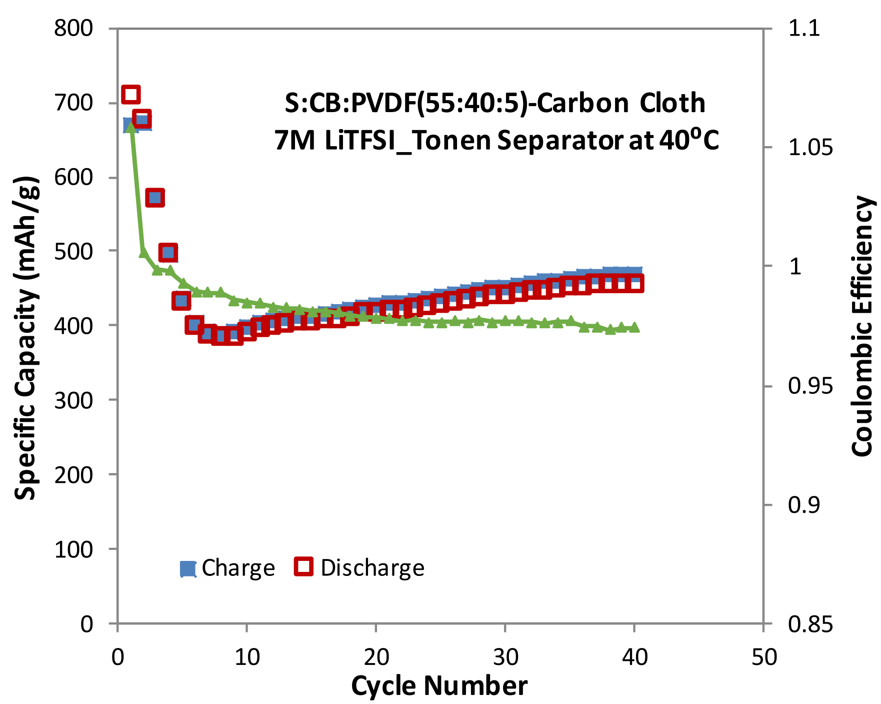
Sulfur Cathode Blended with AlF_3

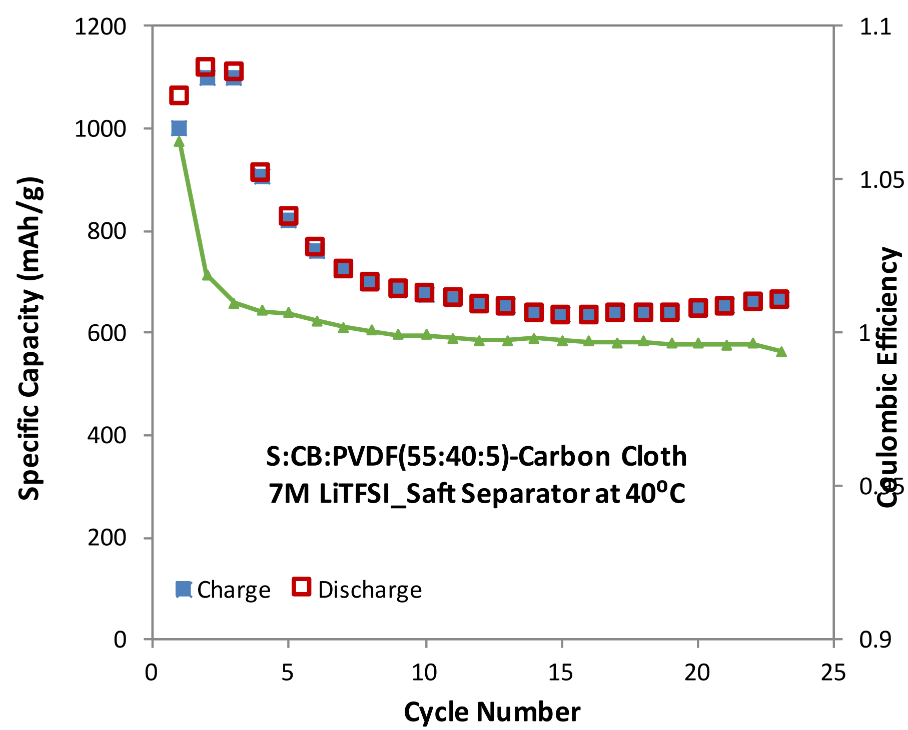




- Good performance (high capacity and efficiency) of Li/S coin cells using AlF_3 blended Sulfur cathode (65% S with 10% AlF_3) at 6 mg/cm^2 loading.
- High area specific capacity is 3 mAh/g per side.

Concentrated Electrolytes

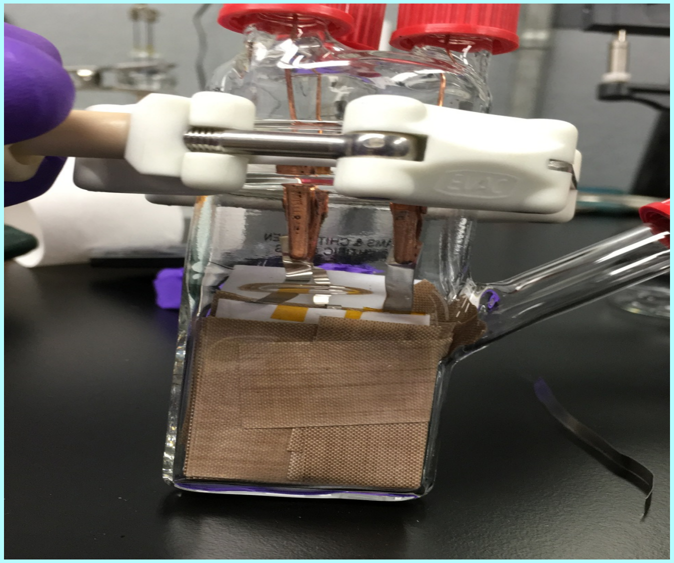




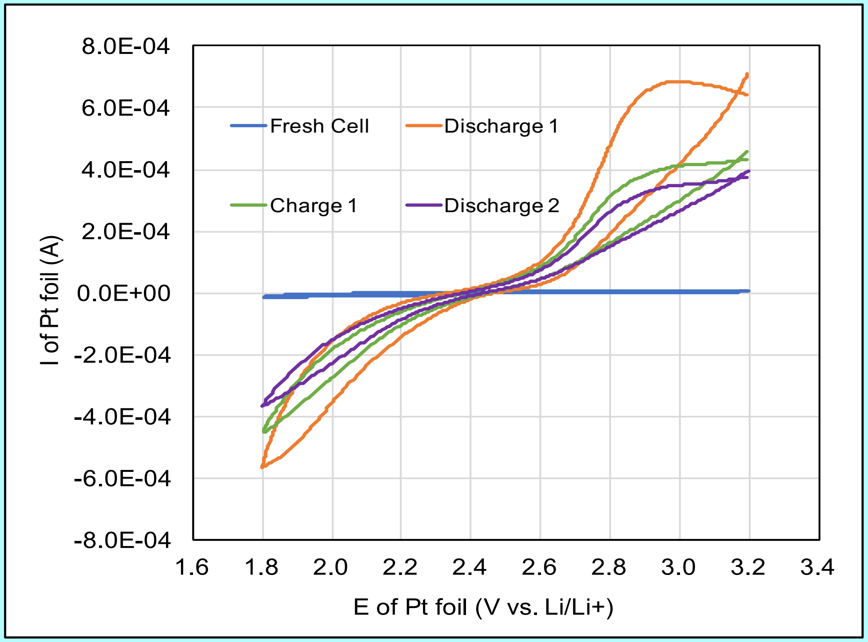
- Highly concentrated electrolytes (solvent in salt) reportedly prevent Li dendrites on the anode and polysulfide shuttle on the cathode.
- Poor performance observed at room temperature in 4M-7M solutions (poor conductivity)
- Slightly improved performance at 40°C with interestingly high coulombic efficiency. May be an option for low power long-life applications.

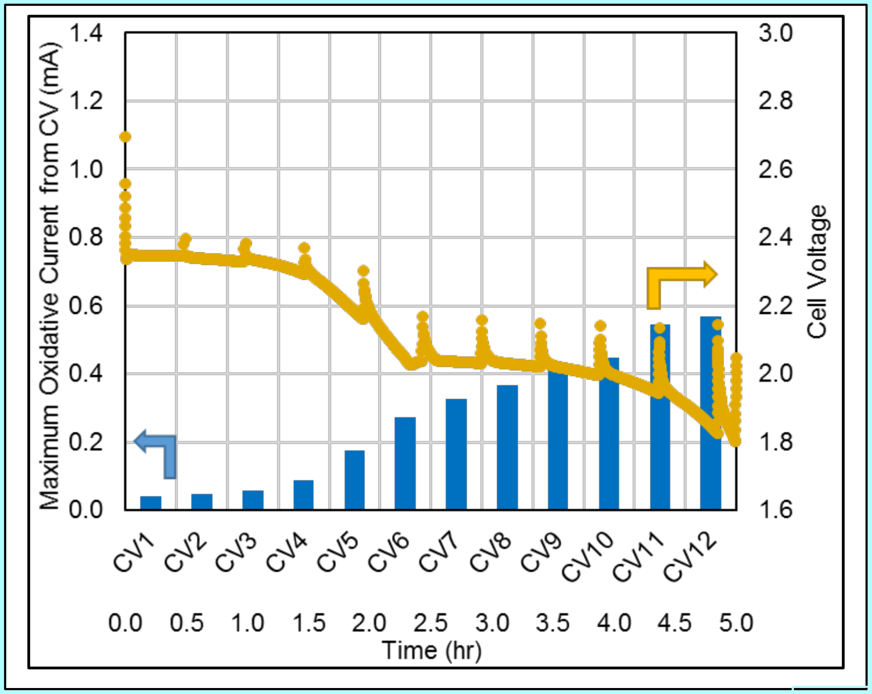
Liumin Suo, Yong-Sheng Hu, Hong Li, Michel Armand and Liquan Chen, “A new class of Solvent-in-Salt electrolyte for high-energy rechargeable metallic lithium batteries”, NATURE COMMUNICATIONS | 4:1481 | DOI: 10.1038/ncomms2513 | www.nature.com/naturecommunications

Four-Electrode Li-S cells for Polysulfide Estimation

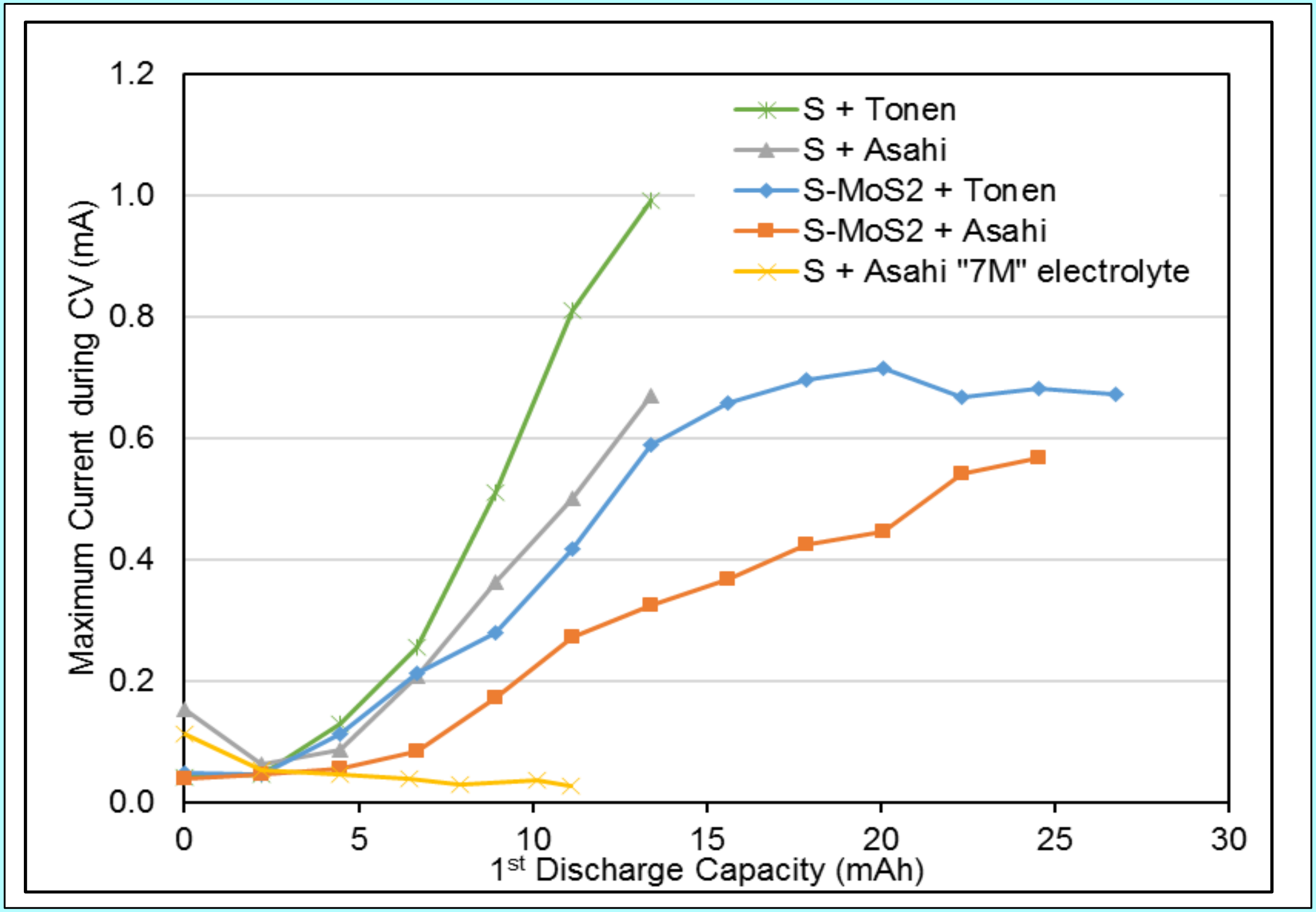


- Four-electrode glass prismatic cell to quantify polysulfides through cyclic voltammetry (right)





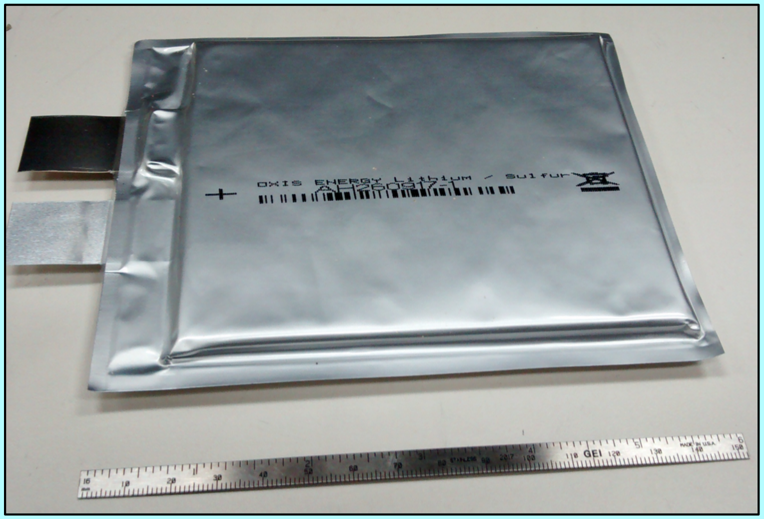
Comparison of Polysulfides with different separators/cathodes

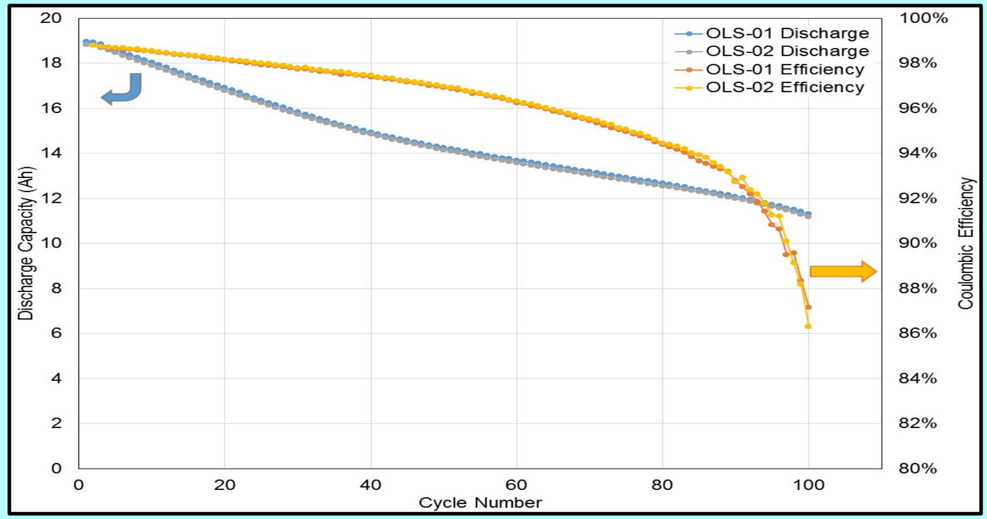


- Polysulfides estimated from CV: S + Tonen > S + Asahi > S+MoS_2 + Tonen > S+MoS_2 +Asahi > S + Asahi + 7M salt
- Cycle life follows the inverse trend

Li/S Prototype Cells from Oxis Energy

- Ten 20 Ah cells received from Oxis and are being tested at JPL





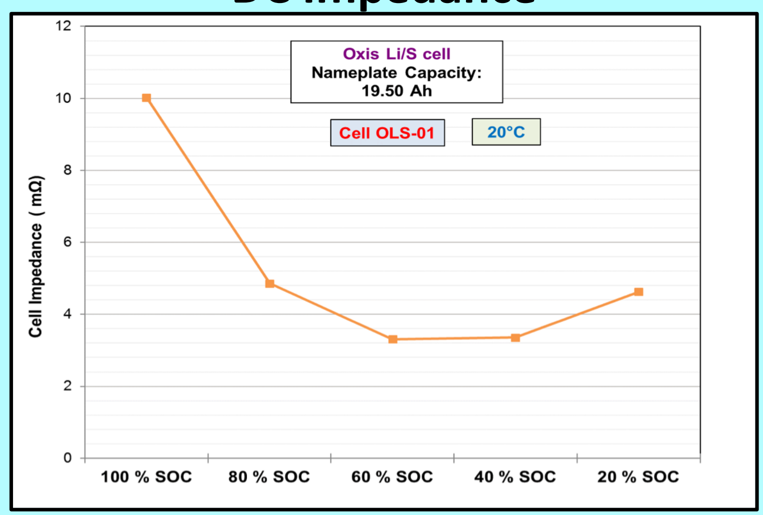
Capacity retention and coulombic efficiency at $C/5$ charge/discharge rates at 20°C.

Cell ID	Mass (g)	1 kHz Z (mΩ)	OCV
AH260917-1	140.131	3.042	2.187
AH260917-2	139.500	3.001	2.185
AH260917-3	140.195	2.995	2.185
AH260917-4	140.105	2.920	2.185
AH260917-5	140.832	3.058	2.186
BM260917-1	139.809	2.817	2.185
BM260917-2	140.179	2.886	2.183
BM260917-3	140.078	2.888	2.185
BM260917-4	140.115	2.893	2.185
BM260917-5	140.989	2.927	2.186
Average:	140.193	2.943	2.185
Stdev:	0.412	0.074	0.001

Self Discharge

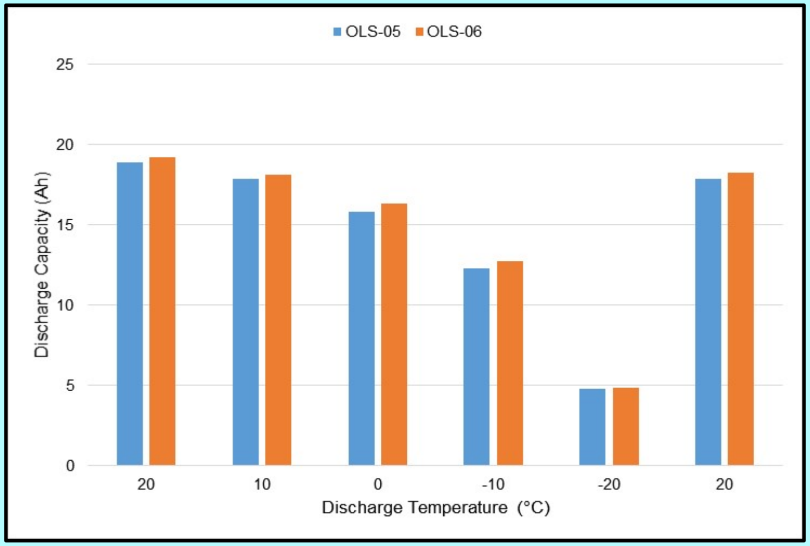
	OLS-03	*OLS-04*
Initial capacity (Ah)	19.08	19.01
Capacity after 1 week (Ah)	17.03	16.75
Self-discharge (%)	10.8%	11.9%

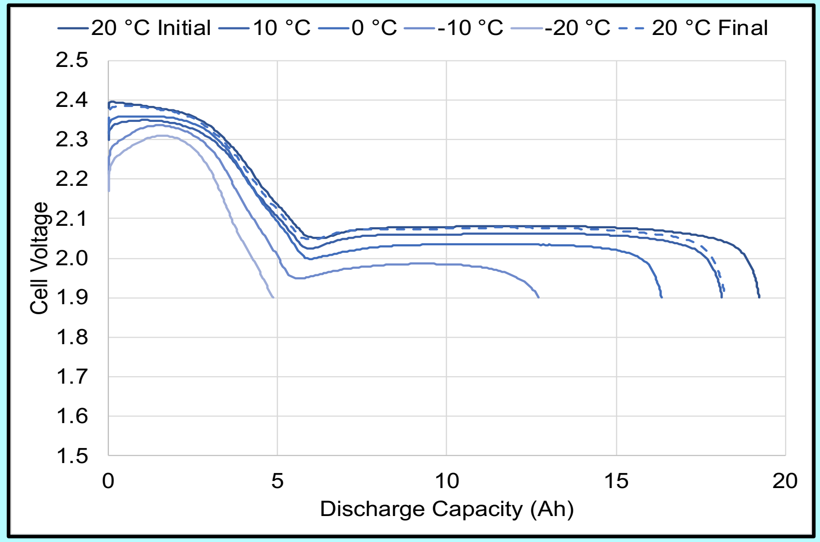
DC Impedance

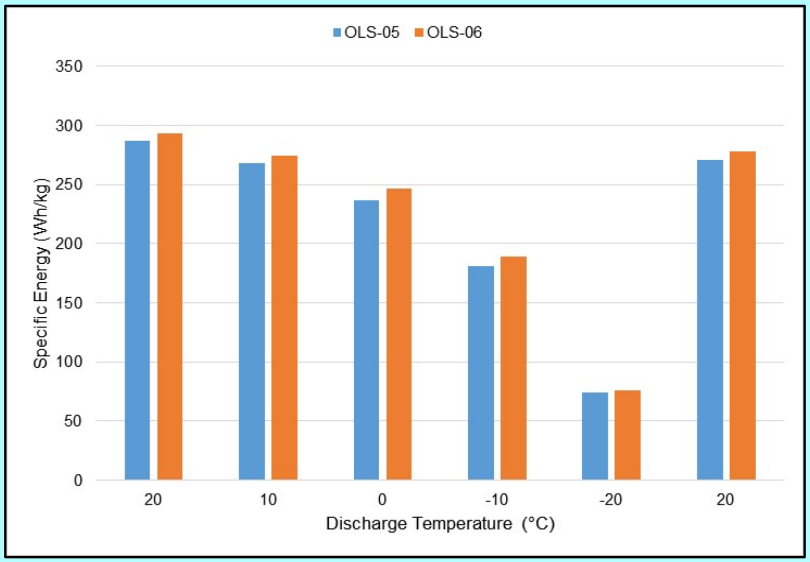


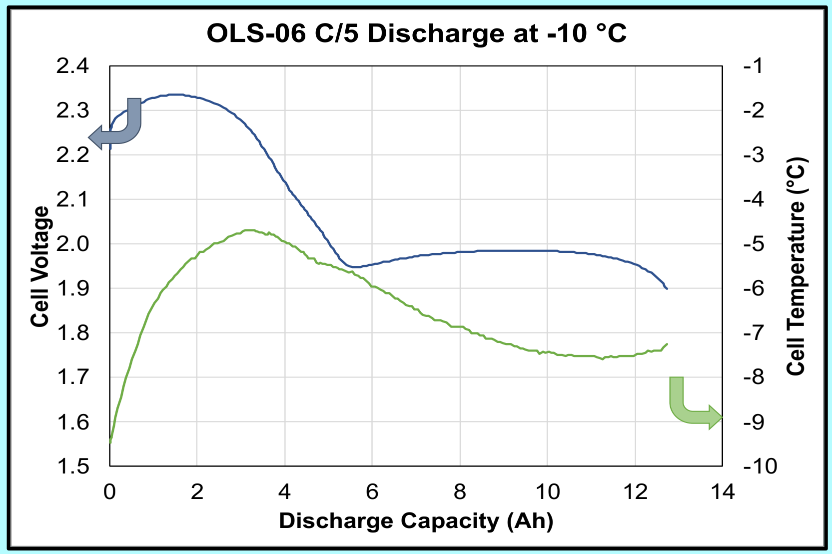
Li/S Prototype Cells from Oxis Energy

Performance vs. Temperature









Capacity and specific energy at *C*/5 discharge rate at various temperatures. After each discharge, the cells were equilibrated at 20 °C and charged at *C*/5 rate before the next discharge. The second set of 20°C data correspond to observed performance after the indicated discharges down to -20°C.

Summary

- Novel sulfur/metal sulfide (TiS_2 and MoS_2) and sulfur composite cathodes display high capacity of ≥800 mAh/g (based on sulfur content), high coulombic efficiency and good cycle life (>75% retention through 100 cycles of 100% depth of discharge) at C/3 rate.
  - High cathode loadings (11 mg/cm^2 or ~6 mAh/cm^2 per side) were demonstrated in Li-S cells containing composite cathodes with good utilization
  - Result in a high specific energy of 400 Wh/kg in prototype cells.
- Metal sulfide coatings also improve the cycle life by minimizing the polysulfides in the electrolyte.
- New separators with ceramic coating (Al_2O_3 and AlF_3) offer interesting opportunities for further improving in this technology. Will augment the composite sulfur cathodes

Acknowledgements

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